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(71) Applicants:
- **FORD MOTOR COMPANY LIMITED**
  Brentwood, Essex CM13 3BW (GB)
  Designated Contracting States:
  GB
- **Ford Motor Company**
  Dearborn, MI 48124 (US)
  Designated Contracting States:
  ES PT

(72) Inventors:
- **Parachuri, Mohan R.**
  Canton, Michigan 48187 (US)
- **Shangguan, Dong Kai**
  Novi, Michigan 48375 (US)
- **Achari, Achyuta**
  Canton, Michigan 48188 (US)

(74) Representative:
Messulam, Alec Moses
A. Messulam & Co. Ltd.,
43-45 High Road
Bushey Heath, Bushey, Herts WD23 1EE (GB)

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(54) **A solder composition**

(57) A soldered composition formed as a paste by use of a fugitive carrier medium including up to 5-15% (by weight) flux, the solder composition being useful for soldering electronic components and packages to a circuit on a substrate consisting of a low cost thermoplastic or polymer having a heat deflection temperature. The composition comprises: (a) a ternary or binary eutectic powder of the alloy system Sn-Bi-In that melts below the heat deflection temperature, (b) a second powder admixed with the first, the second powder consisting of a tin-based powder that reacts with the first powder at 150°C or less in 15 minutes or less and has a melting temperature above the heat deflection temperature, said powders containing less than .1% Pb as an impurity and being proportioned in a weight ratio of 3:1 to 1:3, and (c) other alloying additives selected from the group of Cu, Ni, Ag, Ce, In, Bi, and Au which enhance the mechanical properties of the soldered joints at elevated temperatures and which do not inhibit metallurgical interactions of the first and second powders during soldering. A method of soldering electronic components to a substrate is also disclosed.

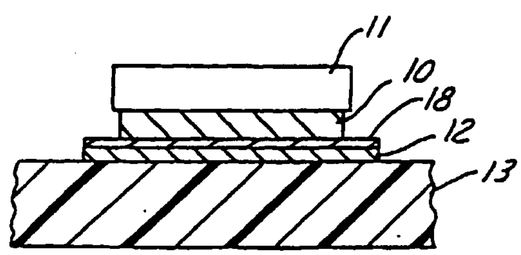

FIG.2

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Description

[0001] This invention relates to a solder composition and more particularly to the use of a multi-component solder paste that has a low melting eutectic first component and a high melting second component that does not melt but does react with the eutectic component during reflow soldering of electronic components or packages to a metallised surface of a thermoplastic or polymer substrate to thereby form a solder interconnect that has a melting temperature higher than the reflow soldering temperature.

[0002] In microelectronic packaging, reflow soldering is one of the last steps in the assembly of the package. The assembly is usually comprised of a substrate prepared with surface metallisation to receive components; the components are constructed with pins, leads or surface metal pads for mounting to the surface metallisation of the substrate. Reflow soldering is a specialised type of soldering using a solid powder in a paste form; the solder paste is deposited at the joint of an assembly to be soldered and the assembly is thereafter heated, such as in an oven to reflow the solder paste as a fluid which, upon cooling, forms a metallurgical bond with the parts to be joined. Reflow soldering is predominately used to attach components to printed circuit boards because of component density, process ease, and improved through-put.

[0003] If the circuit board or substrate is comprised of a low cost thermoplastic material (such as polypropylene (PP), nylon, polycarbonate (PC), acrylonitrile-butadiene-styrene (ABS), polyethylene terephthalate (PET), polypropylene oxide (PPO), or polymethylstyrene (PS)), the chemistry of the solder must be modified to form a reliable solder joint during reflow soldering at a temperature below the heat deflection temperature of such thermoplastic material to avoid damage to such substrate. The heat deflection temperature of such plastic (defined herein to mean the temperature at which a specified deflection occurs in a plastic exposed to a relatively low stress level under controlled conditions) is usually in the range of 100-150°C. Eutectic solder compositions are known which will melt at such lower temperatures; examples of such solders include Sn-Bi (melting at 139°C), Sn-In (melting at 118°C), and Sn-Bi-In (having eutectics melting respectively at 77.5°C, 59°C and 56.5°C). Unfortunately, such lower melting eutectic solders will either melt or significantly soften when exposed to high service temperatures and, as such, the solder interconnect can be completely ruptured under thermomechanical loading in service.

[0004] Therefore there is a need to design a solder and devise a fabrication technique using such solder, that forms a solder joint between the component and substrate at a temperature below the heat deflection temperature of the thermoplastic substrate, but which solder has a post-reflow solder melting temperature which is much higher to preserve the mechanical integrity of the assembly particularly in an automotive service application. To satisfy each such requirement, the solder must possess multiple components that are different in composition and melting temperature.

[0005] Two component solders that have been used by the prior art have been designed to accelerate the wetting of the joint area by early melting of one or more low temperature components, but requires all components to fully melt during completion of the reflow soldering process. Sometimes the reflow soldering may take place in stages where the low temperature component is melted in a first stage, and then a second reflow soldering stage is undertaken to melt the high temperature component and thereby complete the total reflow soldering sequence. In all of the above circumstances, such solders fail to provide both a low temperature reflow melting temperature (below that of the heat deflection of the thermoplastic substrate.) and a post reflow melting temperature (well above the heat deflection temperature of the substrate) that is never experienced during fabrication or service.

[0006] The invention, in a first aspect, is a solder composition formed as a paste by use of a fugitive carrier medium including up to 5-15% (by weight of the composition) flux, the solder composition being useful for soldering electronic components and packages to a circuit on a substrate consisting of low cost thermoplastic or polymer having low heat deflection temperatures. The composition comprises: (a) a first ternary or binary eutectic powder or alloy of the system Sn-Bi-In, (b) a tin based second powder that reacts with the first powder at or below 150°C in 15 minutes or less, said powders containing less than .1% Pb as an impurity and the first powder being weight proportion to the second powder in a ratio of 3:1 to 1:3, and (c) other alloying additives selected from the group of Cu, Ni, Ag, Ce, In, Bi, and Au added in an amount that enhances the mechanical properties of the soldered joints at elevated temperatures and does not inhibit metallurgical interactions of the first and second powders.

[0007] The invention in another aspect is a method of interconnecting electronic components and packages to circuits on a substrate by reflow soldering, the substrate being comprised of a low cost thermoplastic or polymer having a pre-determined heat deflection temperature. The method comprises the steps of: (a) mixing a solder paste formulation consisting of a first ternary or binary eutectic powder of the alloy system Sn-Bi-In, a tin-based second powder that reacts with the first powder at or less than 150°C in 15 minutes or less, and other alloy powder additions that do not inhibit the metallurgical interactions of such first and second powders, the weight ratio of first to second powders being generally 3:1 to 1:3; (b) applying the solder paste onto a faying surface of the substrate circuit; and (c) heating the assembly to a temperature above the melting point of the low temperature eutectic powder to react Sn with the melted eutectic to form solid solutions intermetallics and thereby raise the post reflow soldering temperature of the solder to improve mechanical properties of the soldered joint when in service.

[0008] The invention will now be described, by way of example, with reference to the accompanying drawings, in which:

Figure 1 is a ternary phase diagram of the Sn-Bi-In alloy system illustrating the eutectics useful as the low melting component of the solder compositions;
Figure 2 is a highly enlarged schematic illustration of a solder connection made in accordance with this invention;
Figure 3 is a schematic diagram of the multi-component solder material of this invention illustrating its condition prior to reflow heating;
Figure 4 is a schematic diagram, similar to that of Figure 3, illustrating the solder material condition during and as a result of the reflow heating; and
Figure 5 is a schematic diagram similar to Figure 3, illustrating one of the possible microstructures in the solder after completion of reflow heating and cooling.

[0009] In a preferred embodiment as shown in Figure 2, a solder paste 10 in accordance with this invention is employed to form a tin-based essentially lead-free solder connection for mounting electronic components or packages 11 onto a printed circuit or metallised surface 12 of a thermoplastic or polymer substrate 13.
[0010] The substrate is preferably selected from PP, nylon, PC, ABS, PET, PPO and PS plastics, each of which present the problem solved by this invention. Each of these examples has a heat deflection temperature which is in the range of 100-150°C. It is important that during reflow soldering, temperatures should not be experienced that will exceed such heat deflection temperature.
[0011] Particularly in automotive applications, solders for electronic interconnects must possess certain mechanical and physical properties after the soldering steps have been completed. The interconnect must withstand higher temperatures due to subsequent processing or due to service temperatures under which, the assembly is used. The solder should not soften under thermomechanical loading in service, otherwise the electronic connects can be ruptured.
[0012] A soldering paste according to this invention that will reflow at 150°C or lower and yet achieve a higher post reflow soldering melting temperature, comprises intermixed powder components and a fugitive carrier and fugitive flux. One powder component 15 is a low temperature melting eutectic or alloy of the Sn-Bi-In system and the second component 16 is a high temperature melting powder metal selected for example from Sn or alloys of Sn-3.5% Ag, or Sn-10% In-9.5% Bi-0.5% Ag (by weight). The multi-component may also contain (preferably up to 3 wt.%) other alloying elements selected from the group of Cu, Ni, Ag, Ce, In, Bi and Au; such elements should be selected to enhance the mechanical properties of the solder joint at elevated temperatures as long as they do not inhibit metallurgical interactions of the first and second powders (at or less than 150°C in 15 minutes or less). The weight ratio of the first eutectic component to the second component can range generally from 3:1 to 1:3; i.e., the weight % of the first component to the solder can be 25-75%. The powders are sized to a mesh of - 200/ +325 and contain no more than 0.1% by weight lead. Such paste has the powder components dispersed in a liquid vehicle or carrier 17 that contains a flux. One advantage of paste is that it may be conveniently applied to the faying surface 18, for example by stencil printing. After the faying surfaces are arranged in contact with the paste, the assembly is heated to melt the eutectic powder component, whereupon the partly molten solder coalesces to form a liquid body sufficient to complete the interconnect.
[0013] In order to obtain a strong bond, it is essential that the molten solder flow in intimate contact onto the faying surfaces 18, which phenomena is referred to as wetting. Wetting is enhanced by the presence of the flux, which reacts to remove oxides from the metal surfaces, particularly the faying surfaces. The flux (or flux paste as it is sometimes called) may be comprised of one or more solvents such as high boiling point alcohol, glycol or water, activators such as a rosin or synthetic resin components, weak organic acids, ethoxylated amide compounds, fatty amide compounds, and halides. It may also contain a small percentage of surfactants. The solvents will escape during the reflow heating stage through volatilisation, decomposition or reaction. Depending on the nature of the flux, the flux residue can either be removed during the subsequent cleaning steps or be left on the board for the life of the product.
[0014] Other techniques for applying the solder paste can be used such as screen printing, syringe dispensing, ink jet printing. An alternative method is to coat the second component onto one or both of the parts to be joined and then apply the first component in a paste form.
[0015] Figure 1 shows the various ternary and binary eutectics of the alloy system Sn-Bi-In. Melting temperatures for the eutectics (shown in parentheses) are in degrees Kelvin. When the low temperature powder component is a ternary eutectic, such as E_1 having a melting temperature of 77.5°C, and the high temperature powder component is pure Sn having a melting temperature of 232°C, the intermixed powders will have a reflow melting temperature of about 120°C and a post reflow melting temperature of about 160-180°C, provided the weight ratio between the powders is in the range of 3:2 to 2:3. The differential between the reflow and post-reflow melting temperatures is due to the interaction between unreflowed powder particles and melted powder which forms a single mass consisting of solid solutions 20 and intermetallics 21.

[0016] As shown in Figure 3, prior to reflow heating the powder particles 15 (low temperature powder) can be clearly distinguished as independent, but uniformly mixed with the powder particles 16 (high temperature component), in a carrier or solvent along with the flux. Notice that the particles size of each of the powders will vary (-200/ +325 mesh). During reflow heating (see Figure 4), the low temperature particles will melt and form a liquid 19 and the carrier solvent and flux will escape; the solid particles 16 will interact with the liquid 19. After cooling from reflow heating the microstructure of the solder will consist of uniformly distributed Bi-phase particles 20 in a γ phase eutectic matrix 21. The γ-phase is a Sn-In intermetallic phase with Bi in solid solution. The post reflow melting temperature is determined by the ratio of Sn/E_1 to achieve a temperature of about 160°C, the ratio is generally about 1 (E_1)/1 (Sn).

[0017] Table 1 lists other eutectics of the ternary and binary alloy system that may be used for the eutectic powder component; the table also lists the accompanying melting temperature, composition by weight percent, and the phases for each of said eutectics. Table 1 illustrates that (i) a solder paste consisting of Sn and E_2, E_3 or e_7 or e_4 powders, will reflow in the temperature range of 80-150°C, (ii) a solder paste consisting of pure Sn and one of the Bi-In binary eutectics, such as e_1, e_2, or e_3, will have a reflow temperature in the range of 80-150°C, (iii) a solder paste consisting of pure Sn and Sn-In eutectic (e_6), will have a reflow temperature in the range 140-180°C, (iv) a solder paste consisting of Sn-Bi (e_5) and Sn-In (e_6) eutectics will have a reflow temperature in the range 140-180°C. Any of the above solder pastes may be formulated to substitute Sn-Ag eutectic particles (96.5% Sn-3.5% Ag by weight) or Sn-10%In-95% Bi-0.5% Ag. in place of the Sn particles. Furthermore any of such previously mentioned soldered pastes may also be alloyed with additions of copper, nickel, silver, cerium, bismuth, indium and gold powders in small quantities which can be added to any of such combinations to further improve mechanical properties of the solder at elevated temperatures. These additional elements should preferably be incorporated in an amount only up to 3% by weight of the solder, but not in an amount that would inhibit metallurgical interactions of the first and second powders at or less than 150°C in 15 minutes or less at such temperature.

[0018] A method of using the unique solder composition of this invention in a reflow soldering process to interconnect electronic components or packages to circuits on a thermoplastic substrate, would comprise the following steps: (a) The solder composition is formulated and prepared by admixing metal powders with a flux medium containing 85-95% by weight of the metal powders to form a paste. The solder will consist of dispensable material containing a low melting powder component comprised of a ternary or binary eutectic or alloy of the Sn-Bi-In system, and a high melting component comprising Sn. They are admixed in a ratio with the first component being 25-75% by weight of the admixture, to attain the desired post reflow melting temperature. The solvents, activators and surfactants may be as previously described. (b) The prepared solder paste is applied onto the faying surfaces of the electronic assembly to be soldered (the faying surfaces being typically a copper trace which is overlaid or cast in place on or in a 3-dimensional plastic moulded component or other polymeric or ceramic substrate). The dispensing is carried out by screen printing, stencilling or by syringe application or other dispensing methods. (c) The assembly, containing the deposited solder, is then heated in an oven to a temperature above the melting point of the low temperature metal powder constituent while being essentially below 150°C. The second powder component (Sn) interacts with the melted eutectic during reflow which promotes a higher post reflow melting temperature of the solder and thereby improve the mechanical properties of the solder joint.

TABLE 1

Sn-Bi-In Ternary Eutectic and Bi-In, Sn-In, Sn-Bi Binary Eutectic Compositions			
Eutectic	Eutectic Temperature	Composition (wt.%)	Phases, Melting Temperature and Solid Solubility Ranges
E_1	350.5K 77.5C	18.0Sn 57.2Bi 24.8In	Bi (271.4C) BiIn (110C) γ (Sn-In) (120-224C) (73.5-85.5 wt. % Sn)
E_2	332K 59C	16.5Sn or 19.6 32.5Bi 31.6 51.0In 48.8	β (In-Sn) (120-149C) (12.4-44.8 wt.%Sn) $BiIn_2$ (89.5C) γ (Sn-In) (120-224C)

TABLE 1 (continued)

Sn-Bi-In Ternary Eutectic and Bi-In, Sn-In, Sn-Bi Binary Eutectic Compositions			
Eutectic	Eutectic Temperature	Composition (wt.%)	Phases, Melting Temperature and Solid Solubility Ranges
E_3	329.5K 56.5C	10.0Sn 45.2Bi 44.8In (approximate)	Bi_3In_5 (88.9C) $BiIn_2$ (89.5C) γ (Sn-In) (120-224C)
e_7	335K 62C	13.5Sn 42.0Bi 44.5In	γ $BiIn_2$
e_4	359K 86C	15Sn 55Bi 30In (approximate)	γ BiIn
e_1	382.7K 109.7C	67.4Bi 32.6In	Bi (271.4C) 0-0.005 wt. % In BiIn (110C) 35.4 wt% n
e_2	361.7K 88.7C	50Bi 50In	Bi_3In_5 (88.9C) 47.5-47.97 wt. % In $BiIn_2$ (89.5C) 52.5-53.5 wt. % In
e_3	345.7K 72.7C	33.3Bi 66.7In	$BiIn_2$ (89.5C) 52.5-53.5 wt. % In In (156.6C) 86-100 wt. % In
e_6	393K 120C	49.1Sn 50.9In	γ (224C) 73-85 (appr.) wt. % Sn β (130C) 12.4-448 wt. % Sn
e_5	412K 139C	43.0Sn 57.0Bi	Sn (232C) 0-21 wt. %Bi Bi (271.4C) 0-0.1 wt. % Sn

Claims

1. A solder composition for soldering electronic components and packages (11) to a printed circuit substrate (12,13) consisting of a low cost thermoplastic or polymer selected from polypropylene, nylon, polycarbonate, acrylonitride butadiene styrene, polyethylene terephthalate, polypropylene oxide and polystyrene, each of which has a heat deflection temperature in the range 100 to 150°C, such solder composition being formed as a paste by use of a fugitive carrier medium including a fugitive flux and comprising:

(a) a first powder component consisting of a ternary or binary eutectic or alloy of the system SN-Bi-In that melts below said heat deflection temperature of the thermoplastic or polymer of the substrate, and

(b) a second powder component having a melting point above the heat deflection temperature of the thermoplastic or polymer of the substrate, admixed with the first powder component, said second powder component consisting of a tin-based powder which is capable of reacting with the first powder at 150°C or less in 15 minutes or less to form a reaction product that has a melting temperature above the heat deflection temperature of the thermoplastic or polymer of the substrate, the weight ratio of the first powder to the second powder in the composition being 1:3 to 3:1.

2. A solder composition as claimed in claim 1 including other alloying additions selected from the group Cu, Ni, Ag, Ce, In, Bi and Au which further enhance the post reflow mechanical properties of the solder at elevated temperatures and which does not inhibit metallurgical interactions of the first and second powders during reflow soldering.

3. The composition as in claim 2, in which said alloying additions are limited to 3% by weight of the solder.

4. The composition as in any preceding claim, in which the second powder is selected from the group of Sn, Sn-3.5% Ag, and Sn-10% In-9.5% Bi-0.5% Ag.

5. The composition as claimed in any preceding claim, in which said second powder is pure Sn having a melting temperature of 232°C, and the first powder component is the eutectic E_1 selected from the phase diagram of Figure 1 having a melting temperature of 77.5°C, said composition having a post reflow melting temperature of about 150-180°C.

6. The composition as claimed in any one of claims 1 to 4, in which the first powder component is the eutectic E_2 selected from the phase diagram of Figure 1.

7. The composition as claimed in any one of claims 1 to 4, in which the first powder component is the eutectic E_3 selected from the phase diagram of Figure 1.

8. The composition as claimed in any one of claims 1 to 4, in which the first powder component is the eutectic e_1 selected from the phase diagram of Figure 1.

9. The composition as claimed in any one of claims 1 to 4, in which the first powder component is the eutectic e_2 selected from the phase diagram of Figure 1.

10. The composition as claimed in any one of claims 1 to 4, in which the first powder component is the eutectic e_3 selected from the phase diagram of Figure 1.

11. The composition as claimed in any one of claims 1 to 4, in which the first powder component is the eutectic e_4 selected from the phase diagram of Figure 1.

12. The composition as claimed in any one of claims 1 to 4, in which the first powder component is the eutectic e_5 selected from the phase diagram of Figure 1.

13. The composition as claimed in any one of claims 1 to 4, in which the first powder component is the eutectic e_6 selected from the phase diagram of Figure 1.

14. The composition as claimed in any one of the preceding claims in which the particle size for each of the first and second powders is -200/+325 mesh.

15. The composition as claimed in any one of the preceding claims containing less than 0.1% of Pb by weight of the composition.

16. A method of soldering electronic components or packages (11) to a printed circuit substrate (12,13) consisting of a low cost thermoplastic or polymer selected from polypropylene, nylon, polycarbonate, acrylonitride butadiene styrene, polyethylene terephthalate, polypropylene oxide and polystyrene, each of which has a heat deflection temperature in the range 100 to 150°C;

providing a solder composition as a paste in a fugitive carrier medium including a fugitive flux and comprising:

(a) a first powder component consisting of a ternary or binary eutectic or alloy of the system Sn-Bi-In that melts below said heat deflection temperature of the thermoplastic or polymer of the substrate;
(b) a second powder component having a melting point above the heat deflection temperature of the thermoplastic or polymer of the substrate, admixed with the first powder component, said second powder component consisting of a tin-based powder, the weight ratio of the first powder to the second powder in the composition being 1:3 to 3:1;

applying the prepared solder paste on to the fraying surfaces of the printed circuit substrate and electronic components or packages; and heating the applied solder paste to a temperature above the melting point of the first powder component but below the heat deflection temperature of the substrate to form a solder joint and to form metallurgical interactions with the second powder component, thereby raising the post reflow melting temperature of the solder composition.

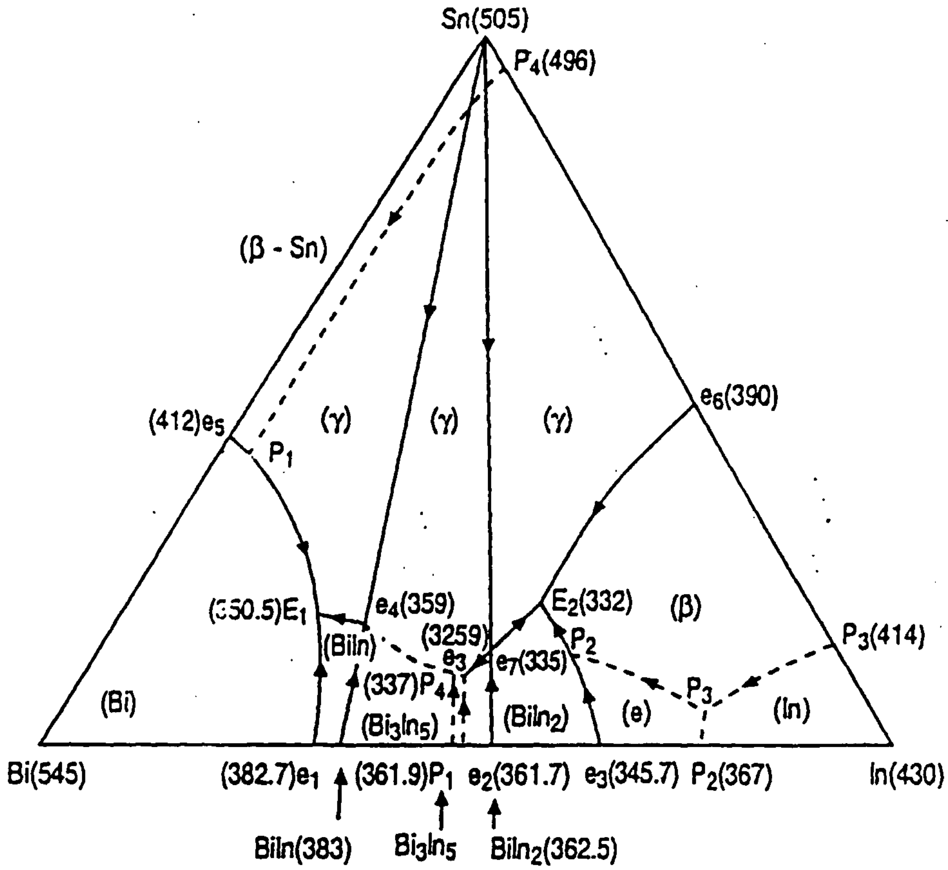
Sn(505)
P4(496)
(β - Sn)
(412)e5
P1
(γ)
(γ)
(γ)
e6(390)
e4(359)
E2(332)
(β)
(BiIn)
(3259)
e3
e7(335)
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FIG.1

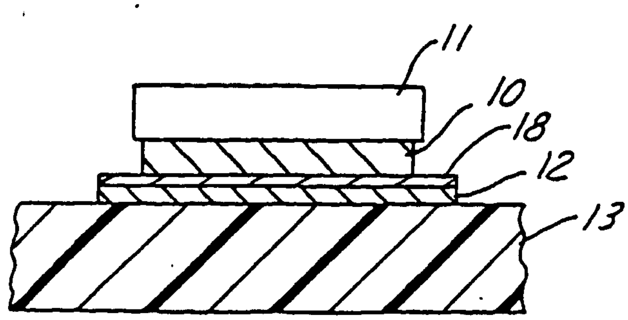
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FIG.2

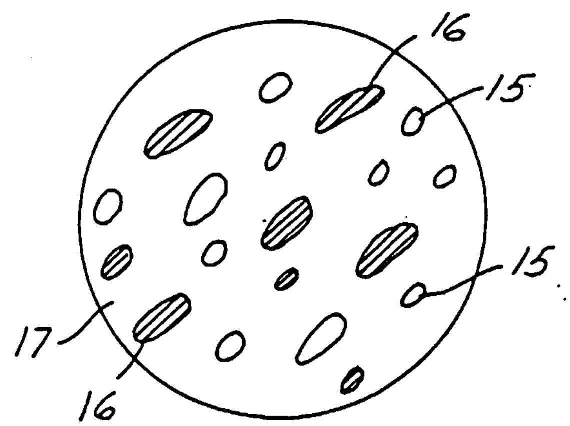

FIG.3

(DURING REFLOW)

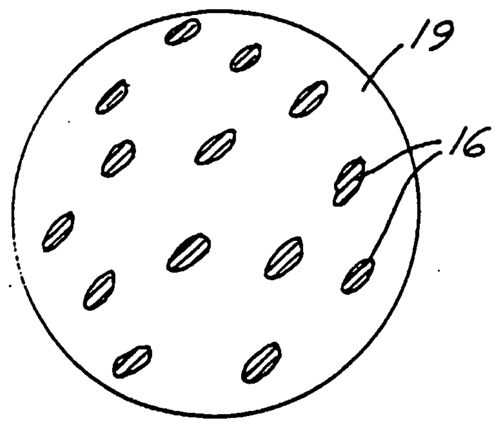

FIG.4

(AFTER REFLOW)

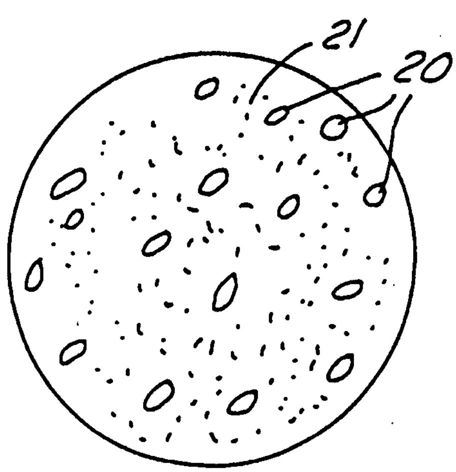

FIG.5

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 00 12 2960

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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	19 January 2001	Mollet, G

CATEGORY OF CITED DOCUMENTS

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